EUROPEAN COMMISSION

bcr information

REFERENCE MATERIALS

Certification of the content of chlorinated hydrocarbons sorbed on TENAX GR®

BCR-555

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ABSTRACT

A reference material related to the measurement in air of chlorinated hydrocarbons by polymer sorption and analysis by thermal desorption - gas chromatography has been produced.

Each unit consists of a stainless steel tube, 9 cm in length and of 5 mm inner diameter, packed with 250 mg of Tenax GR charged with controlled amounts of dichloromethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene and toluene.

The material has been tested for homogeneity and stability; the amount of each compound desorbed from a unit is certified on the basis of measurements in 6 laboratories.

The certified values and uncertainties are given below. Uncertainties are expressed as expanded uncertainties (coverage factor k = 2) according to the Guide for Expression of Uncertainties in Measurement [5].

Compound	CAS	Certified value in ng	Uncertainty in ng (k=2)
Dichloromethane	[75-09-2]	320	40
Perchloroethene	[127-18-4]	327	17
Toluene	[108-88-3]	57	7
1,1,1-Trichloroethane	[71-55-6]	370	40
Trichloroethylene	[79-01-6]	390	40

LIST OF ABBREVIATIONS AND SYMBOLS

BCR	Community Bureau of Reference
CHC	Chlorinated hydrocarbons
CRM	Certified Reference Material
DCM	Dichloromethane
EU	European Union
FID	Flame ionisation detector
GC	Gas Chromatography
IRMM	Institute for Reference Materials and Measurements (Geel, Belgium)
MS	Mass Spectrometry
MSD	Mass selective detection
n	Number of measurements
PER	Perchloroethylene
PTFE	Polytetrafluoroethylene
RM	Reference Material
RSD	Relative standard deviation
SD	Standard deviation
s_{meas}	Measurement uncertainty
TCE	1,1,1-Trichloroethane
TOL	Toluene
TRI	Trichloroethylene
U	Uncertainty
u_{bb}	Uncertainty component from homogeneity
u^*_{bb}	Upper limit of inhomogeneity that can be hidden by the method repeatability
$u_{c,bb}$	Combined uncertainty of the homogeneity study
u_{char}	Uncertainty component from batch characterisation
U_{CRM}	Expanded uncertainty of CRM (k=2)
U_{exp}	Expanded uncertainty (k=2) of the stability tests, calculated from the contributions of the calibration procedure and the standard deviation of the analyses.
u_{lts}	Uncertainty component from long-term stability
u_{sts}	Uncertainty component from short-term stability

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1. INTRODUCTION

Although evidence exists that some chlorinated hydrocarbons may be formed by natural processes, their presence in the air is almost exclusively of anthropogenic origin. Chlorinated hydrocarbons (CHC) are still widely used as industrial solvents (dichloromethane, chloroform, 1,1,1-trichloroethane), degreasing agents (trichloroethene), scavengers in gasoline (1,2-dichloroethane), dry cleaning agents (perchloroethene) and as intermediates in various production processes.

Most volatile CHC are harmful or toxic by inhalation, some of them classifying as (possible) carcinogenic or teratogenic agents (dichloromethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane). Moreover, CHC are well known to contribute to the degradation of ozone in the stratosphere as well as to the formation of ozone in the troposphere.

Measurements of concentrations of CHC in the air provide the basis for:

- assessment of compliance with air quality standards;
- assessment of human exposure;
- examination of sources and faiths;
- validation of measurement methods;
- dispersion modelling;
- dose/concentration - effect relationships;
- epidemiology.

In all these cases, only valid measurement results will lead to reliable conclusions. Although it is to be expected that the use of CHC will eventually decrease as a result of the implementation of the Montreal Protocol [1], measurements will still be necessary if only to check compliance with the demands of the Protocol.

Methods used for measuring concentrations are predominantly based on pre-concentration on a suitable sorbent, desorption and analysis by gas chromatography. Sorption onto polymer sorbents, either by pumped or diffusive methods, followed by thermal desorption represents an optimum in methodology, as it combines ecology (no desorption solvents used), economy (reusable samplers, automation), detectability (whole-sample analysis, generally 100% desorption efficiency, no disturbance by solvent peaks) and flexibility (large variation in sorbents available).

The need to produce a certified reference material for the determination of chlorinated hydrocarbons by thermal desorption - gas chromatography was first established in an experts' meeting organised by BCR in September 1988. There, it was decided to prepare and certify a reference material for air measurements of CHC based on polymer sorption and analysis by thermal desorption - gas chromatography.

2. PARTICIPANTS

Throughout the project, many laboratories have participated in the various intercomparisons described below (chapter 3). At the start of the project, all laboratories have received a numerical code for reasons of confidentiality. The numbering has remained unchanged during the course of the project. The following laboratories (listed in alphabetical order) have participated in the certification project.

Co-ordination

- NMi Van Swinden Laboratory, Delft , The Netherlands.

Provision and preparation of materials

- NMi Van Swinden Laboratory, Delft , The Netherlands.

Homogeneity studies

- NMi Van Swinden Laboratory, Delft , The Netherlands.

Stability studies

- NMi Van Swinden Laboratory, Delft , The Netherlands.

Statistical Evaluation

- NMi Van Swinden Laboratory, Delft , The Netherlands.
- European Commission, DG RTD (formerly DG XII, Standard Measurements and Testing Programme), Rue de la Loi 200, B-1040 Brussels, Belgium.
- European Commission, DG JRC, IRMM, Retieseweg, B-2440 Geel, Belgium.

Certification analyses

Six laboratories participated in the study. They are listed below in alphabetical sequence, which does not correspond with the laboratory identification numbers used.

- Arbejdsmiljøinstituttet, Copenhagen, Denmark;
- Bundesanstalt für Arbeitsschutz, Dortmund, Germany;
- Health & Safety Laboratory, Sheffield, United Kingdom;
- Landesamt für Umweltschutz und Gewerbeaufsicht Rheinland-Pfalz, Mainz, Germany;
- Landesumweltamt Nordrhein Westfalen, Essen, Germany;
- VTT, Espoo, Finland.

3. PRELIMINARY STUDIES

3.1 Introduction

Before the start of the actual certification project a series of activities were undertaken in order to enable the preparation and certification of a reference material for CHC. The work on the feasibility of the preparation of a certified reference material related to the determination of chlorinated hydrocarbons (CHC) started in 1988. The work focused on:

- the selection of a suitable sorbent and suitable preparation conditions for the reference material;
- the agreement between calculated spiking levels and results of analyses of the reference material;
- the agreement between the analytical results of different laboratories.

Within the course of these activities, a number of additional problems were revealed, the solution of which was essential for the success of the certification project.

3.2 Chronological description of activities

In 1988, the first suitability tests of polymers sorbents suitable for a CHC reference material were performed by TNO [2]. In a one-year stability study, two sorbents were tested that were considered from previous experience to be candidate materials, i.e., Chromosorb 102® and Tenax TA®. These sorbents were spiked with 1,1,1-trichloroethane, trichloroethene and perchloroethene from a dynamically generated standard atmosphere at levels of approximately 1 µg each, a composition considered by experts as representative of an average air sample of chlorinated hydrocarbons.

The stability study clearly indicated that Tenax TA was the better of the two sorbents, with recoveries after one year of 96% or better [3]. The material consisting of the above CHC sorbed on Tenax TA was tested in February/March 1989 in an intercomparison. 12 EU laboratories with prior experience in the certification of BCR-112 (benzene, toluene and m-xylene on Tenax TA) participated in this exercise.

The analytical results showed an unexpectedly large scatter, particularly for 1,1,1-trichloroethane. Here, breakthrough in the preparation of calibration standards was found to be the cause of many deviating results. Purging volumes used in preparation procedures of calibration standards by liquid spiking were in excess of the sorbent's breakthrough volume. Moreover, the theoretical amount of 1,1,1-trichloroethane present on the sorbent, calculated from the spiking procedure used, was found to deviate considerably from the results found by the participants. Here, the volume of standard atmosphere used to spike the samples (10 l per g of sorbent) was considered to be close to or in excess of the breakthrough volume of the sorbent for 1,1,1-trichloroethane, resulting in partial breakthrough. The results for trichloroethylene and perchloroethylene were more satisfactory. After omission of technically explicable outliers, a reasonable agreement between results was found.

In a second intercomparison, held in January/February 1990, the spiking volume used to prepare the samples was reduced to 5 l per g of sorbent; nevertheless, breakthrough of 1,1,1-trichloroethane to an extent of 28% was observed. This finding indicated that Tenax TA is in principle less suitable as a sorbent for 1,1,1-trichloroethane.

In this intercomparison also an apparent systematic difference was found between results from laboratories using calibration standards either prepared by liquid spiking or by gas phase spiking

in the absence of a solvent, i.e., from standard atmospheres. The former procedure was suggested to yield lower CHC responses due to suppression ('*quenching*') of the flame-ionisation detector response by the residual methanol present in the calibration standard (note that complete removal of the solvent would almost certainly lead to losses of 1,1,1-trichloroethane, as explained above).

Alteration of GC split ratios as a result of the presence of methanol was named as another possible cause of deviations.

These hypotheses were tested in a third intercomparison fully dedicated to the study of the effects of calibration techniques used. In this intercomparison, utmost care was given to the elimination of other factors possibly responsible for interlaboratory variances.

All preparation procedures were such that traceability to primary standards of mass and volume was ensured, meaning that:

- all volumetric glassware (including syringes) was calibrated with the solvent used by repetitive weighing on a calibrated analytical balance;
- the purities of all compounds used were confirmed;
- the purge volumes used to charge the tubes were minimised in order to avoid compound breakthrough.

In addition, toluene was used as 'internal standard' in these experiments since the correct calibration for toluene had been proven feasible in the certification of BCR-112 [3].

The results of these experiments, performed in April/May 1990, again showed a lack of conformity, not only between laboratories, but also between the various standard preparation techniques.

Therefore, the effect of the presence of methanol on the FID response to chlorinated hydrocarbons was studied. To this end, calibration standards were prepared

• from a dynamically generated standard atmosphere of dichloromethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene and toluene;

• from a dynamically generated standard atmosphere containing a large excess of methanol (equivalent to the amount of methanol required for the production of a standard by spiking with 5 µl of a methanol solution).

The standards were subsequently analysed, resulting in FID response factors relative to toluene given in Table 1 below.

Table 1 - FID response factors for CHC relative to toluene

Compound	FID Response Factor relative to Toluene mean ± standard deviation (n=5)	
	Without methanol	With methanol
Dichloromethane	0.135 ± 0.004	0.135 ± 0.004
1,1,1-Trichloroethane	0.188 ± 0.006	0.194 ± 0.007
Trichloroethene	0.209 ± 0.007	0.201 ± 0.006
Perchloroethene	0.164 ± 0.004	0.161 ± 0.005

From these results it may be concluded, that the presence of methanol in the calibration standards has no significant effect on the FID response factors of the chlorinated hydrocarbons. Hence, the apparent differences between FID responses of calibration standards prepared by different techniques cannot be attributed to the presence of methanol, but are probably coincidental.

In view of the problems with breakthrough of the more volatile CHC when using Tenax TA as the sorbent, in 1991/1992 a second sorbent feasibility study was performed with the sorbents Chromosorb 106, Tenax GR, Carboxen 569 and Carbosieve SIII, the first being a high-surface area styrene-divinylbenzene copolymer, the second the graphitized version of Tenax TA, and the latter two graphitized molecular sieves. The sorbents were selected on the basis of their reported sorption capacities for volatile CHC such as dichloromethane and 1,1,1-trichloroethane.

A one-year stability test of dichloromethane, 1,1,1-trichloroethane, trichloroethylene and perchloroethylene sorbed in amounts of approximately 1 µg each, led to the unequivocal conclusion that Tenax GR was the better of the four sorbents, although again some breakthrough was observed of dichloromethane and 1,1,1-trichloroethane (a spiking volume of 4 l per g of sorbent was used).

Chromosorb 106 suffered from severe blank development, while recovery of trichloroethylene and perchloroethylene decreased considerably upon storage. Recoveries from Carbosieve SIII and Carboxen 569 on storage decreased considerably upon storage [4].

In the frame of the certification project, a fourth intercomparison was organised in November/December 1993 with the aim of assessing the feasibility of the certification of a reference material consisting of 250 mg Tenax GR in a 9 cm x 5 mm ID stainless steel thermal desorption tube sealed using a teflon ferrule with brass fittings and end caps.

For this intercomparison, tubes were spiked with dichloromethane, 1,1,1-trichloroethane, trichloroethene and perchloroethene in amounts of 450 to 520 ng using a spiking volume of 2.4 litres of air per gram of sorbent

All participants received five samples from a batch of 250, of which the homogeneity had previously been established and three sample blanks, together with a standard report form. All results submitted were analysed for within and between laboratory variance, and were the subject of a discussion meeting.

As in previous intercomparisons, a relatively large scatter in results was observed. This was due mainly to the fact that the variance between laboratories was much higher than the variance within laboratories. From the discussion of the individual results the calibration procedures used were found again to be the main sources of error. It was concluded that the organisation of an intercomparison aimed at certification in that present situation was not feasible.

It was therefore decided to organise a fifth intercomparison aimed at demonstrating analytical proficiency of the participating laboratories similar to the above fourth intercomparison.

In the fifth intercomparison, the compound levels were lowered to 240 to 300 ng, while 42 ng of toluene was added as an internal standard for the calibration procedures used (*vide supra*). This intercomparison was held in April/May 1994.

Similar to the fourth intercomparison, a lack of between-laboratory consistency was observed with results of some laboratories still deviating considerably from the calculated spiking levels.

On the basis of '*interlaboratory*' consistency of results in the last two intercomparisons (overlap of 95% confidence intervals of mean values reported) and consistency of the 95% confidence intervals with the theoretical charging levels of the compounds, nine laboratories were selected for participation in the certification intercomparison. Of these, 6 laboratories eventually participated.

3.3 Conclusions

The work preceding the actual preparation and certification of the reference material for CHC has led to the conclusion that Tenax GR is suitable as the sorbent for the reference material. A material consisting of 1 µg each of dichloromethane, 1,1,1-trichloroethane, trichloroethylene and perchloroethylene sorbed on 250 mg Tenax GR was demonstrated to be stable for at least one

year. Systematic effects due to compound breakthrough could be avoided by reducing the volume of standard atmosphere spiked to 2.4 l/g of sorbent.

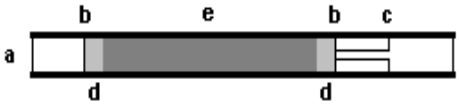
The results of subsequent intercomparisons that were organised confirmed the need for the production of a CRM for the analysis of CHC. A considerable number of laboratories were found to have problems with these analyses resulting in large between-laboratory variances. This finding confirms the need for a certified reference material for the determination of CHC using thermal desorption - gas chromatography.

A group of nine laboratories using diverse calibration and analytical techniques was found to produce results that were both in mutual agreement and in agreement with the calculated spiking levels of the samples. These laboratories were selected for participation in the certification intercomparison.

4. PRODUCTION OF THE REFERENCE MATERIAL

4.1 Description of the tubes

The tubes used for the production of BCR-555 were commercial stainless steel tubes filled with Tenax GR as shown schematically in Figure 1.



a. Stainless steel tube 90 mm length * 6.24 mm outer diameter / 5 mm inner diameter
b. Stainless steel gauze
c. Spring
d. Quartz wool plug
e. Bed of Tenax GR (250 mg)

Figure 1 - Scheme of TENAX-filled tubes used for the certification of BCR-555

The tubes were capped with brass swagelok end caps containing one-piece PTFE ferrules. Before packing the tubes, the Tenax GR was thermally cleaned by heating at 300 °C for 16 hours while purging with a stream of purified helium.

After packing, all tubes were thermally cleaned by heating at 250 °C for 20 hours while purging with a stream of purified helium. 10% of the cleaned tubes were checked for their blank levels. These were found to be below 1% of the charging levels of the CHC and toluene.

The batch of BCR-555 consisted of 600 tubes.

4.2 Description of the charging procedure

Diffusion cells were used to blend known mass flows of dichloromethane, 1,1,1-trichloroethane, trichloroethene, perchloroethene and toluene into a known flow of purified air, delivered through a calibrated mass flow controller.

The compounds used in the diffusion cells were of stated purities better than 99%, and were dried over molecular sieve before use. The absence of volatile impurities at levels >0.1% was confirmed by headspace gas chromatography with flame-ionisation detection.

A known, fixed volume of this standard atmosphere was drawn through each sample tube by mass flow control. The spiking volume was determined by calibration of the mass flow controllers using a mercury piston meter to a flow of 50.0 ± 0.05 ml/min and by the use of electronically timed operation of the three-way valves used in the charging facility. A schematic representation of this facility is given in Figure 2.

All units of BCR-555 tubes were spiked on September 15, 1995 by the Chemistry Department of the Nederlands Meetinstituut Van Swinden Laboratory. The tubes were spiked in 50 series of 12 (the facility has 12 sampling points, permitting the simultaneous spiking of 12 tubes).

Of each series of 12 tubes spiked simultaneously, one was selected for homogeneity testing such that all sampling points were subsequently chosen (i.e., sampling point 1 for series 1, 13, 25, 37

and 49, sampling point 2 for series 2, 14, 26, 38 and 50, sampling point 3 for series 3, 15, 27, and 39, etc.).

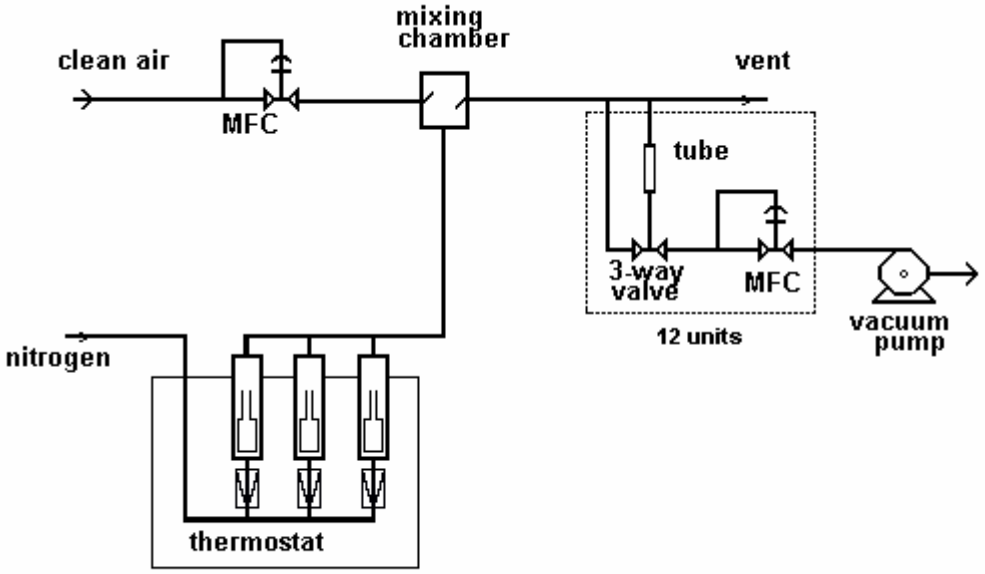


Figure 2 - Schematic representation of the standard atmosphere generation and charging facility

The following quality control measures were taken to ensure the constant level of charging:

- the temperatures of the diffusion cells were controlled to within ± 0.02%;
- all mass flows of air were controlled to within ± 0.2%;
- all tubes were charged within a 13-hour period in which the atmospheric pressure (which influences the release rates of the diffusion cells) varied only marginally;
- the volume of air drawn through each tube was fixed by application of an electronic timer operating all three-way valves in the sampling rack;
- the volume of air drawn through each tube was restricted to 2.4 l per g of sorbent in order to minimize breakthrough of dichloromethane and 1,1,1-trichloroethane; the occurrence of some breakthrough of these compounds cannot be excluded, however.

The calculated amounts of dichloromethane, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene and toluene charged onto the tubes are 325, 375, 383, 325 and 57 ng, respectively.

The total uncertainty in these amounts is composed of the uncertainties associated with:

- impurities of the compounds used (estimated by assumption of a rectangular uncertainty distribution);
- background levels of the nitrogen and air used as carrier and diluent gases;
- determination of the mass flows of the diffusion cells;
- temperature variations of the diffusion cells;
- measurement of and variations in the atmospheric pressure;
- measurement of the temperatures of the standard atmosphere and the laboratory;
- determination of air mass flow rates;

- determination of the sampling time.

The total (expanded; k=2) relative uncertainty is calculated as twice the square root of the quadratic summation of the standard deviations associated with the uncertainty components given above and is found to be 1.7%.

It should be kept in mind, however, that the uncertainties for dichloromethane and 1,1,1-trichloroethane may be enhanced due to the occurrence of component breakthrough.

5. TESTING OF THE REFERENCE MATERIAL

5.1 Homogeneity testing

The homogeneity of the batch of 600 samples of BCR-555 was ascertained by analysis of 50 tubes, one from each series of 12 simultaneously charged tubes (see 4.2).

The analyses were performed by the Chemistry Department of the Nederlands Meetinstituut Van Swinden Laboratory on September 15/16 of 1995 using an automated thermal desorption system coupled with a gas chromatograph equipped with a flame ionisation detector and a fused-silica capillary column. Thermal desorber and gas chromatographic settings are given in Table 2.

Table 2 - Settings for thermal desorber and gas chromatograph

Thermal desorber settings	
Desorption temperature (°C)	250
Desorption time (min)	5
Desorption flow (ml/min)	16
Cold trap	Tenax GR -30 °C low, 300 °C high
Cplitter	none used
Transfer line temperature (°C)	180
Gas chromatograph settings	
Column	VOCOL 60 m * 0.75 mm id; d_f = 1.5 µm
Temperature programme	5 min at 40 °C, 10 °C/min to 250 °C
Carrier gas	helium, 100 kPa pressure
Detector	FID 300 °C

No calibration of the responses was performed in view of the objective of the test, namely the determination of homogeneity expressed as the coefficient of variation of the absolute responses observed. The tests were performed immediately after the production of the batch of BCR-555 in the order of production (no randomisation of selected samples). In this way, a possible 'drift' in the charging levels as a function of time may be observed from the analytical results, provided that instrument drift is absent. The results of the homogeneity test are presented in Table 3.

The precision of the mean peak areas is given as both absolute and relative standard deviations. These comprise the random errors resulting from the charging of the tubes and the analyses. The results indicate that all relative standard deviations are below 3%, thereby indicating a satisfactory homogeneity of the batch of charged tubes. From the responses as a function of time, it can be concluded that no trend is detectable in the charging levels as a function of the time of production.

Although the observed variations are certainly an over-estimation of the uncertainty resulting from the residual inhomogeneity of the CRM, $u_{c,bb}$, - as it contains also the measurement variability - the relative standard deviations of Table 3 are included in the uncertainty budget of BCR-555 (see Chapter 6.3.1).

Table 3 - Results of the homogeneity test for BCR-555

	Response (area in mV.s)				
	DCM	TCE	TRI	TOL	PER
	4267	7735	7690	5935	5199
	4274	7887	7867	6207	5425
	4285	7921	7961	6251	5475
	4230	7864	7821	6043	5374
	4355	8000	7983	6244	5460
	4342	8027	8104	6301	5514
	4343	7988	7984	6252	5480
	4291	7681	7935	6217	5466
	4173	7579	7919	6164	5419
	4239	7442	7914	6146	5437
	4213	7300	7857	6151	5430
	4187	7659	7937	6185	5438
	4246	7724	7959	6230	5491
	4345	7709	7987	6194	5496
	4159	7466	7993	6174	5452
	4286	7644	7957	6194	5483
	4136	7652	7986	6158	5498
	4148	7638	7854	6067	5298
	4163	7450	7918	6126	5444
	4232	7938	8000	6017	5490
	4097	7926	7975	6166	5507
	4238	7811	8017	6174	5570
	4211	7600	7965	6202	5559
	4234	7614	8023	6157	5479
	4061	7491	7745	5949	5313
	4209	7619	8004	6182	5541
	4235	7681	8086	6197	5476
	4273	7957	8030	6197	5538
	4268	7562	8006	6067	5515
	4255	7503	8039	6117	5517
	4261	7548	7956	6130	5479
	4280	7950	8089	6263	5593
	4285	7909	7970	6188	5456
	4261	7857	8023	6192	5560
	4298	7903	8120	6253	5614
	4439	7712	8038	6151	5468
	4195	7882	8084	6187	5557
	4199	7945	8131	6245	5597
	4189	7938	8084	6254	5572
	4257	7638	7926	6092	5444
	4180	7619	7998	6026	5470
	4288	7612	8019	6184	5492
	4291	7620	8128	6219	5567
	4140	7460	8053	6149	5542
	4264	7934	8104	6209	5596
	4104	7698	8063	6193	5582
	4202	7643	8024	6154	5544
	4214	7756	8111	6239	5592
	4186	7829	8126	6251	5642
	4155	7693	8104	6245	5609
Mean	4234	7724	7993	6170	5495
SD	72	178	95	78	84
RSD (%)	1.7	2.3	1.2	1.3	1.5

5.2 Stability testing

The testing of the stability of BCR-555 was performed annually over a period of 3 years. For this purpose, samples have been stored at approximately –20°C, room temperature (20°C ± 0.5°C) and approximately 40°C, respectively. One and two years after preparation, BCR-555 was subject to stability tests, in which five samples for each storage temperature were analysed.

Calibration was performed with standards at 3 levels bracketing between 0.9 and 1.1 times the certification values. The calibration standards were freshly prepared by sampling from standard atmospheres generated from diffusion cells using a procedure similar to that applied for the preparation of the batch of BCR- 555 (see 4.2). The results of this test are presented in Tables 4-9. Data presented are:

- results of the individual analyses;
- means and relative standard deviations of these results;
- mean recovery for one compound calculated as the ratio of the mean absolute result and the certification value;
- expanded uncertainty of the test, calculated from the contributions of the calibration procedure and the standard deviation of the analyses as twice the square root of the quadratic sum of the associated standard deviations.

Table 4 - Results of one-year stability test at 40 °C. All results are expressed in ng

Tube nr	DCM	TCE	TRI	TOL	PER
1717	304	382	376	61	328
1489	303	383	377	55	340
1765	308	387	377	55	329
1244	313	376	372	53	327
1384	301	357	360	52	315
Mean	306	377	372	55.2	328
Mean recovery (%)	97.1	103.3	96.0	97.9	100.2
RSD (%)	1.6	3.2	1.9	6.0	2.6
U_{exp} (%)	3.8	6.7	4.4	12.2	5.6

Table 5 - Results of two-year stability test at 40 °C. All results are expressed in ng

Tube nr	DCM	111-TCE	TRI	TOL	PER
1230	307	394	388	55	334
1882	301	403	387	53	333
1150 *	83	335	359	70	324
1661	295	392	396	58	335
1505	303	400	401	59	343
Mean	302	397	393	56	336
Mean recovery (%)	95.8	108.8	101.3	99.6	102.9
RSD (%)	1.7	1.2	1.7	4.8	1.4
U_{exp} (%)	3.9	3.2	3.9	9.8	3.4

* Not included in calculation because of apparent loss of sample

Table 6 - Results of one-year stability test at room temperature. All results are expressed in ng

Tube nr	DCM	TCE	TRI	TOL	PER
1599	336	364	376	55	328
1575	316	379	376	52	327
1033	314	366	373	54	325
1762	303	373	371	55	331
1640 *	258	327	331	60	280
Mean	317	370	374	54.0	328
Mean recovery (%)	100.7	101.5	96.4	95.8	100.2
RSD (%)	4.3	1.9	0.7	2.4	0.7
U_{exp} (%)	8.9	4.2	2.5	5.2	2.6

* Not included in calculation because of apparent loss of sample.

Table 7 - Results of two-year stability test at room temperature. All results are expressed in ng

Tube nr	DCM	TCE	TRI	TOL	PER
1481	311	392	397	59	340
1416	306	398	391	57	335
1210	309	404	420	61	335
1049	312	399	395	58	329
1880	316	404	399	60	336
Mean	310	398	401	58.9	335
Mean recovery (%)	98.7	109.4	105.7	104.6	102.4
RSD (%)	2.6	1.3	3.3	2.4	1.4
U_{exp} (%)	2.6	3.8	6.8	4.9	2.7

Table 8 - Results of one-year stability test at -20 °C. All results are expressed in ng

Tube nr	DCM	TCE	TRI	TOL	PER
1580	337	361	376	55	330
1628	311	364	361	54	321
1133	336	355	370	54	327
1374	324	356	369	54	327
1805	324	340	355	52	310
Mean	326	355	366	53.8	323
Mean recovery (%)	103.6	97.3	94.3	95.4	98.7
RSD (%)	3.3	2.6	2.3	2.3	2.5
U_{exp} (%)	6.9	5.5	5.0	4.9	5.3

Table 9 - Results of two-year stability test at -20 °C. All results are expressed in ng

Tube nr	DCM	111-TCE	TRI	TOL	PER
1072 *	308	416	451	104	345
1624	299	402	391	60	332
1710	314	397	393	58	335
1860	307	398	400	61	337

Tube nr	DCM	111-TCE	TRI	TOL	PER
1402 *	309	393	430	87	339
Mean	306	399	395	60	335
Mean recovery (%)	97.3	109.3	101.7	105.6	102.4
RSD (%)	2.5	0.7	1.3	2.9	0.8
U_{exp} (%)	5.3	2.4	3.2	6.2	2.5

* Samples contain spurious peaks with responses far in excess of compounds responses; results are not included in the calculation of the means because of possible interferences in integration.

For all compounds at each temperature of storage, the uncertainty intervals of the determined concentrations and the certified values are overlapping. Hence, no statistically significant decrease in concentrations is observable. From this, it may be concluded that the material is stable upon storage for two years, even at an increased temperature of 40 °C. At this temperature, however, compound loss may be promoted by loosening of the end caps of the samples.

Also some samples stored at -20 °C in a freezer suffer from contamination from a hitherto unknown source. Based on comparison with pure compounds available in the laboratory, the contaminant is likely to be a branched hexane (probably 3-methylpentane). Therefore, it is recommended that samples are stored at room temperature in a clean environment; samples should in all cases not stored at sub-zero temperatures due to risk of contamination by inward migration of compounds.

From the data obtained for the storage at room temperature combined with those obtained after 2-years of storage at –20 °C (used as reference values) a shelf-life was plotted. After new confirmation analysis in 2001, the shelf-life plot used this measurement as starting point. For further details, refer to section 6.3.1.

6. BATCH CHARACTERISATION

6.1 Intercomparison

From the batch of BCR-555 remaining after the homogeneity test sets of six were prepared by random selection. To each set, three blank tubes were added. Individual codes of all tubes were registered. The sets of tubes were distributed among the participating laboratories by courier service.

In addition, all participants received a standard form for reporting of results and details of the calibration and analytical and QA/QC procedures used. Participants were instructed to perform all analyses under reproducibility conditions (analysis on separate days with newly prepared calibration standards) and to fully ensure the traceability of the analytical results to primary standards of mass and volume by preparing calibration standards with suitably calibrated equipment and according to traceable preparation procedures.

The analytical methods and the calibration and quality control procedures used are summarised in Tables 10 and 11. It should be noted in addition that all laboratories:

- used calibrants of a confirmed purity of >99%;
- used linear regression to establish calibration curves from the responses of their calibration standards with regression curves fitted without forcing through the origin.

6.2 Discussion of the results

Table 10 - Summary of analytical methods

Lab	Thermal desorption data				GC data		
	Desorber	Desorption time / temperature	Desorption flow (ml/min)	Cold trap packing/ temperature	Column(s)	Temperature programme	Detector (s)
1 [1]	ATD 400	10 min/300 °C	40	Tenax TA 20 mg -30 - 300 °C	DBWax 50m * 0.25 mm 0.5 µm PVMS 50m * 0.32 mm 5 µm	50 °C (10 min) - 8°/min 120 °C (1.2 min) - 20°/min 200 °C (5 min)	FID (2)
6 [2]	ATD 50 (2)	7 min/200 °C 10 min/200 °C	30 10	Tenax -30°C Tenax -30 °C	BP1 50m * 0.22 mm BP10 50m * 0.22 mm	40 - 90 °C 2°/min 50 - 180 °C 5°/min	FID (2) FID (2)
7	ATD 400	10 min/170 °C	10	Tenax TA 20 mg -30 - 300 °C	CPSil 19CB 60m * 0.32 mm 0.25 µm	20°C (1 min) - 4°/min 100 °C - 35°/min 240 °C (10 min)	FID
10	ATD 400	4 min/300 °C	31.5	Tenax GR -30 - 300 °C	DB624 75m * 0.53 mm 3 µm	50 - 95 °C 3 °/min	FID
13 [3]	ATD 400	6 min/260 °C	50	Tenax TA - 30 °C	HP-PONA 50m * 0.2 mm 0.5 µm	40 °C (5 min) - 6°/min 190 °C	MSD (5972) FID

15	ATD 400	15 min/240 °C	30	Tenax TA -30 - 300 °C	DB5 MS 30m * 0.25 mm 1 µm	40 °C (6 min) - 10°/min 200 °C	FID

1. Laboratory 1 used a dual column gas chromatographic system with column inlet splitter

2. Laboratory 6 used two separate ATD-GC systems for analysis, analysing 3 samples on each system. Each GC had a dual column configuration with column inlet splitting.

3. Laboratory 13 used a single-column gas chromatographic system with column outlet splitting and a dual detector system.

6.2.1 Technical discussion

A meeting was organised to discuss the results of the intercomparison. Prior to the meeting, all participants had received an information package consisting of overviews of all results, the results of the statistical evaluation, and details of calibration and analytical procedures used. The results for one sample of Laboratory 13 were excluded as the laboratory indicated a lack of sensitivity of its mass-selective detector when analysing the sample. All results used for certification are presents in tables 12 - 16, with graphical representations of bar graphs and 95% confidence intervals given in figures 3 - 7.

Table 11 - Summary of data on calibration and quality control

Lab	Calibrant preparation			Calibration standard			
	Principle	Medium	Procedure	Sorbent	Spike volume	Purge gas/ flow/ time/volume	Nr of standards per analysis
1	Gas spiking	Air	Standard atmosphere prepared by continuous injection	Tenax GR	5, 10, 15, 20 or 25 ml calibration gas	Not applicable	5
6	Liquid spiking	MeOH	Gravimetric	Chromosorb 106	5 µl		4
7	Liquid spiking	MeOH	Gravimetric	Tenax GR	5 µl		5
10[1]	Liquid spiking Gas spiking	MeOH Air	Gravimetric Standard atmosphere prepared by continuous injection	Tenax GR	5 µl 50, 65, 85 or 100 ml calibration gas	Nitrogen 25 ml/min 4 min	4 standards each at 4 compositions
13	Liquid spiking	MeOH	Gravimetric	Tenax GR	0.98 µl calibrated	Nitrogen 50 ml/min 5 min	5
15	Gas spiking	Air	Standard atmosphere prepared from solution in ethylbenzene by continuous injection	Tenax GR	Gas tight syringe		2 standards each at 3 compositions

1. Laboratory 10 used a combination of liquid and gas phase spiking for the preparation of calibration standards.

Table 12 - Laboratory results for dichloromethane (ng per sample)

Lab number							Mean	CI
1	311.4	257.51	322.31	322.14	316.57	291.14	303.5	26.6
6	296	301	353	279	272	343	307.3	35.1
7	347	366	322	315	285	291	321.0	33.0
10	326.7	315.9	320.1	318.7	325.3	328.6	322.6	5.3
13	252.2	298.2	326.5	299.8	276.8		290.7	34.5
15	342	364	371	325	334	327	343.8	20.4
Charging level	327				Mean of means		315	
					SD		24	
					RSD (%)		7.5	

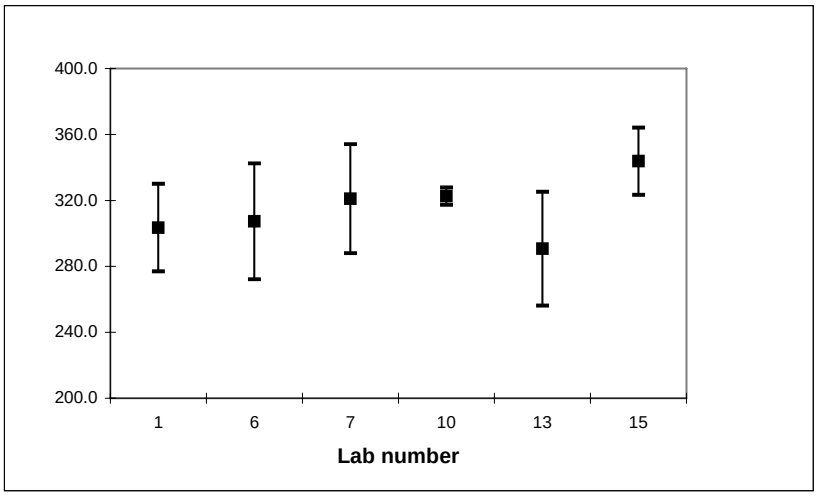


Figure 3 - Bar graphs and 95% confidence intervals for dichloroethane

Table 13 - Laboratory results for 1,1,1-trichloroethane (ng per sample)

Lab number							Mean	CI
1	361.27	353.31	350.87	364.09	351.6	355.28	356.1	5.7
6	383	373	348	382	383	360	371.5	15.3
7	331	359	329	342	334	332	337.8	11.9
10	389.9	384.1	378.3	379.6	365.6	372.1	378.3	9.0
13	348.7	353.6	359.6	368.8	347.1		355.6	11.0
15	382	372	415	402	397	394	393.7	15.9
Charging level	383				Mean of means		366	
					SD		20	
					RSD (%)		5.4	

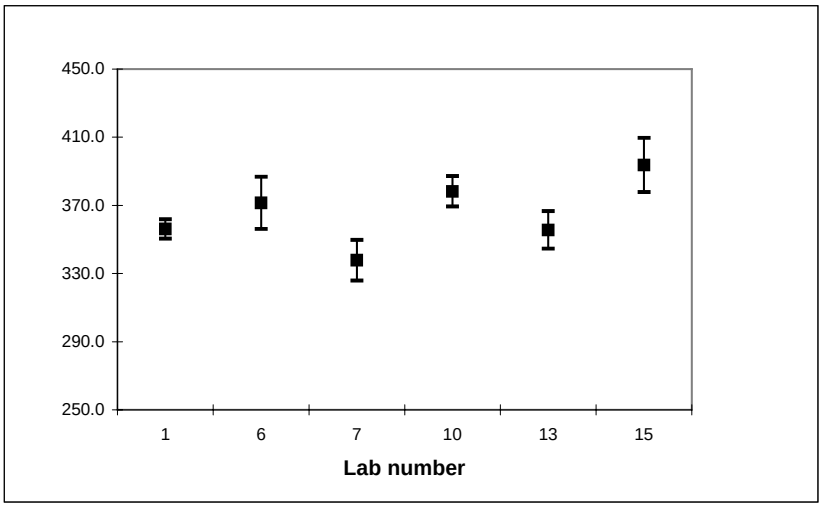


Figure 4 - Bar graphs and 95% confidence intervals for 1,1,1-trichloroethane

Table 14 - Laboratory results for trichloroethylene (ng per sample)

Lab number							Mean	CI
1	372.91	378.01	372.45	372.62	364.51	367.56	371.3	4.9
6	398	389	405	401	393	400	397.7	6.1
7	380	414	386	397	382	361	386.7	18.7
10	376	368.3	388.3	369.3	381.7	389.4	378.8	9.6
13	377.7	381.4	389.9	386.2	399.2		386.9	10.3
15	415	405	420	403	410	392	407.5	10.3
Charging level	388				Mean of means		388	
					SD		13	
					RSD (%)		3.3	

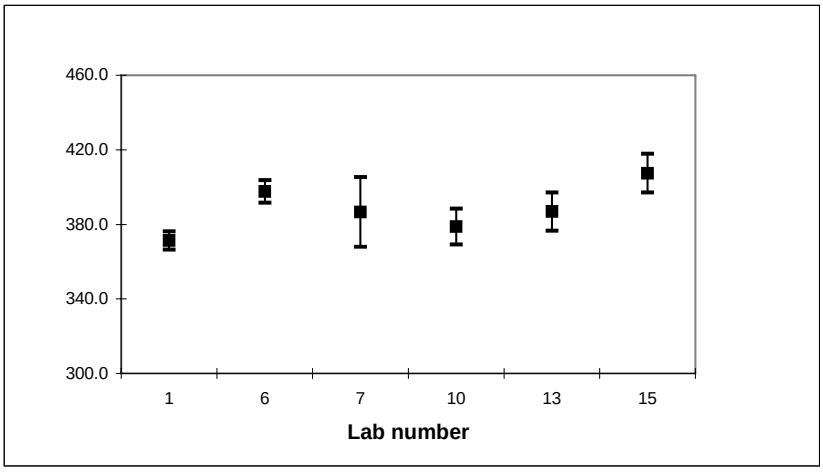


Figure 5 - Bar graphs and 95% confidence intervals for trichloroethylene

Table 15 - Laboratory results for toluene (ng per sample)

Lab number							Mean	CI
1	56.82	66.89	53.83	55.47	51.54	58.2	57.1	5.6
6	57.1	55.3	57.8	55.7	55.2		56.2	1.4
7	50.2	57.5	51	58.6	54.1	51.4	53.8	4.7
10	54.1	55.6	59	54.2	55.2	56.4	55.8	1.9
13	59.1	55.2	55.6	59.5	57.2		57.3	2.4
15	59.7	56	55.4	61	60.4	55.2	58.0	2.8
Charging level	57				Mean of means		56.4	
					SD		1.5	
					RSD (%)		2.6	

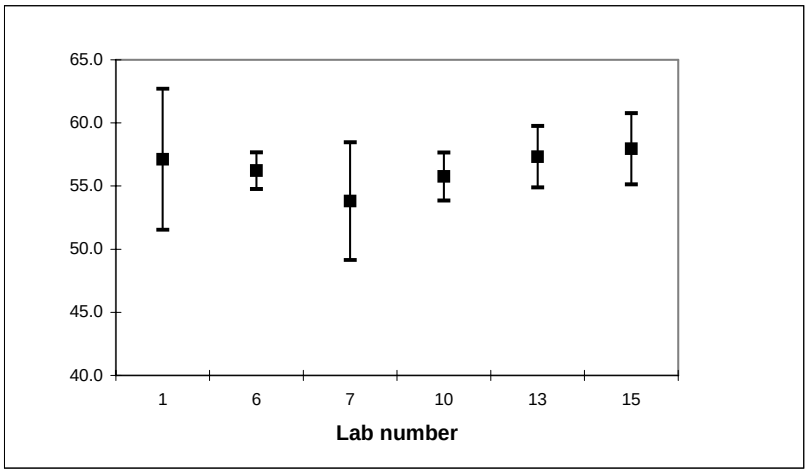


Figure 6 - Bar graphs and 95% confidence intervals for toluene

Table 16 - Laboratory results for perchloroethylene (ng per sample)

Lab number							Mean	CI
1	311.91	317.42	316.69	317.07	305.87	321.28	315.0	5.7
6	333	329	329	343	330	330	332.3	5.7
7	306	339	310	325	311	318	318.2	12.8
10	320	316.3	332.7	316.9	322.9	331.6	323.4	7.5
13	324.7	325.7	332	338	336.6		331.4	7.6
15	349	291	366	343	363	331	340.5	28.8
Charging level	325				Mean of means		327	
					SD		10	
					RSD (%)		2.9	

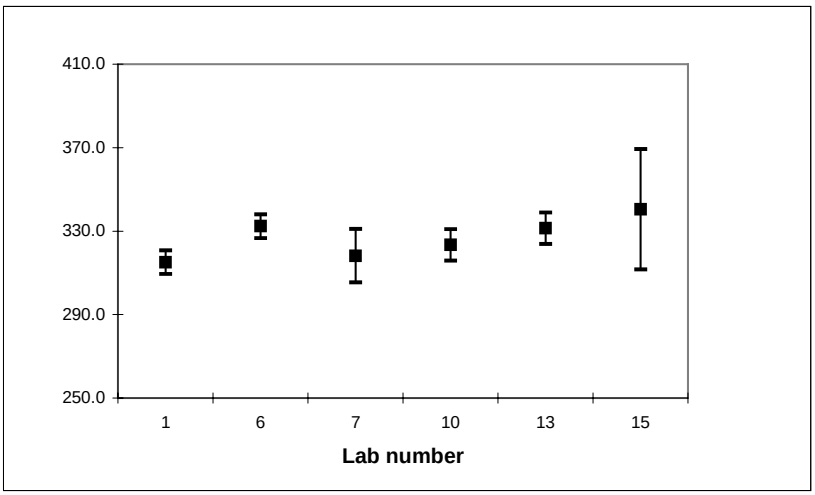


Figure 7 - Bar graphs and 95% confidence intervals for perchloroethylene

6.2.2 Statistical discussion

The data set used for the statistical analysis includes all results with expectance of the results for one sample for Laboratory 13. This data set was used for a statistical analysis including the following tests (all at the 99% level):

- Cochran variance outlier test
- Bartlett variance homogeneity test
- Snedecor F-test
- Kolmogorov-Smirnov-Lilliefors normality of means test
- Nalimov means outlier test.

The results are summarised in Table 17 below.

Table 17 - Results of statistical analysis of certification data set

	DCM	TCE	TRI	TOL	PER
Number of accepted sets	6	6	6	6	6
Number of accepted replicates	35	35	35	33	35
Normality of mean values (Kolmogorov-Smirnov-Lilliefors)	Normal	Normal	Normal	Normal	Normal
Outlying mean values (Nalimov)	None	None	None	None	None
Snedecor F-value	2.97	18.3	9.60	0.930	3.07
Homogeneity of variances (Bartlett)	About homog.	Homog.	Homog.	About homog.	Not homog.
Outlying variances (Cochran)	None	None	None	None	None
Mean value	315	365	388	56.4	327
Standard deviation	18.5	19.7	12.9	1.32	9.63
95% Confidence limits	19.4	20.7	13.6	1.39	10.1

6.3 Certification of BCR-555

It is a basic assumption, when using sorbing agents for measuring that sorption and desorption are quantitative. Tables 12 - 17 show that this condition is met for trichloroethylene, perchloroethylene and toluene. Indeed, the values from the charging data and the analytical results are in good agreement.

For dichloromethane and 1,1,1-trichloroethane the mean levels deviate from the charging values to a greater extent. Moreover, the variability of the analytical results is higher. This may be explained from the fact that Tenax GR is a relatively non-ideal sorbent for these compounds.

However, the assumption of quantitative sorption and desorption was not made *a priori*, so that the certification for these compounds is based on the results of the analyses, with the masses corresponding to the masses *desorbed*.

6.3.1 Uncertainties

The evaluation of uncertainties in the context of certification exercises has evolved over the past decade. Nowadays, certified values should be accompanied by uncertainty statements in compliance with the requirements made by GUM [5]. While the design of new certification projects consider the needs for a proper estimation of the various uncertainty sources such as stability and homogeneity, older campaigns aimed only on qualitative statements (yes/no decisions) whether a material was stable and homogeneous.

The evaluation described hereafter is based on a concept described by Pauwels *et al.* [6 and literature cited] and uses available data discussed in the previous chapters.

6.3.1.1 Concept

Based on the findings obtained in the stability and homogeneity studies as well as the scattering of results in the batch characterisation estimates for u_{bb} (homogeneity), u_{lts} (long-term-stability) and u_{char} (batch characterisation) were obtained and combined according the following equation:

$$U_{CRM} = 2 \cdot \sqrt{u_{bb}^2 + u_{lts}^2 + u_{char}^2}$$

Due to the selected transport conditions selected for dispatch, the uncertainty constituent for short-term stability (u_{sts}) is negligible and consequently not included in the overall uncertainty. The estimation of the other uncertainty sources is described below.

6.3.1.2 Homogeneity

The homogeneity study is exhaustively described in section 5.1. In this particular case, each sample of BCR-555 can only be used once ("*single-shot*" sample). Thus no estimate of measurement variability, s_{meas}, could be obtained. A correction of between-unit variability for this term as requested by the classical BCR-approach is not possible. As a conservative estimate of the uncertainty contribution related to the material's homogeneity , $u_{c,bb}$, the relative standard deviations of Table 3 were used.

6.3.1.3 Stability

As mentioned in section 5.2, long-term stability data obtained after 1 and 2 years storage at room temperature and after 2 years of storage at –20°C (used as reference temperature) were used to arrive at a reasonable quantitative estimate of the uncertainty related to stability, u_{lts}.

The value was u_{lts}, was calculated for a shelf-life of 48 months. The respective expiry date is stated on the certificate of BCR-555 and may be extended, if new evidence for the stability of BCR-555 is available. Based on the observations made during the stability study the reference temperature was shifted from –20°C to +4°C.

Figures 8 - 12 show the respective shelf-life plots for dichloromethane, 1,1,1-trichloroethane, trichloroethylene, toluene and perchloroethylene.

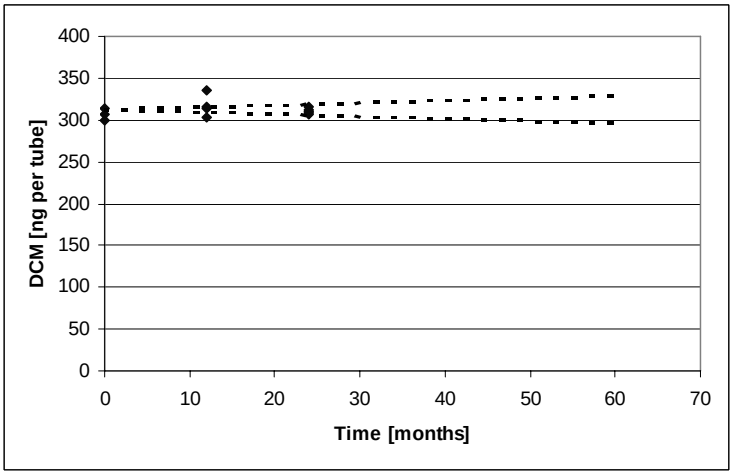


Figure 8 - Shelf-life plot for dichloromethane in BCR-555. For a shelf-life of 48 months u_{lts} was estimated to 4.27 %.

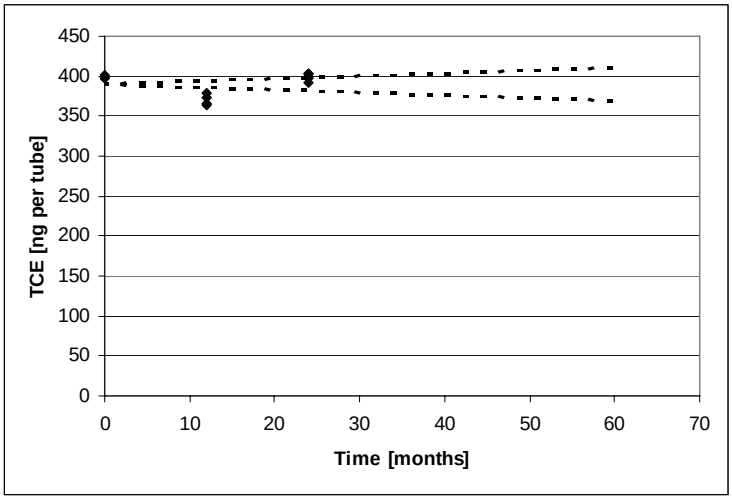


Figure 9 - Shelf-life plot for 1,1,1-trichloroethane in BCR-555. For a shelf-life of 48 months u_{lts} was estimated to 4.35 %.

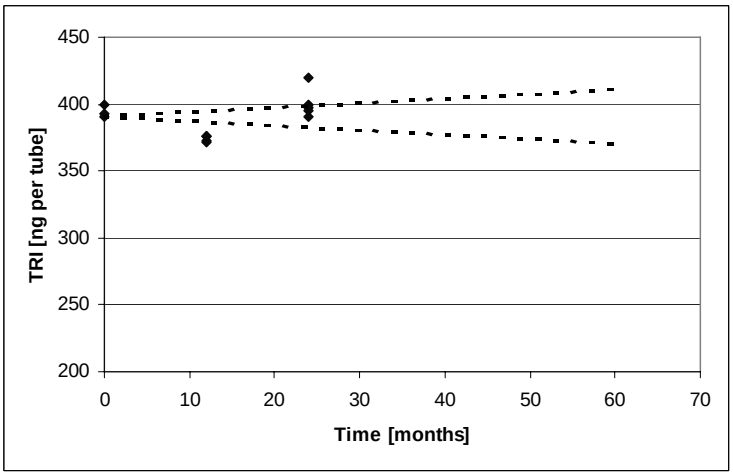


Figure 10 - Shelf-life plot for trichloroethylene in BCR-555. For a shelf-life of 48 months u_{lts} was estimated to 4.11 %.

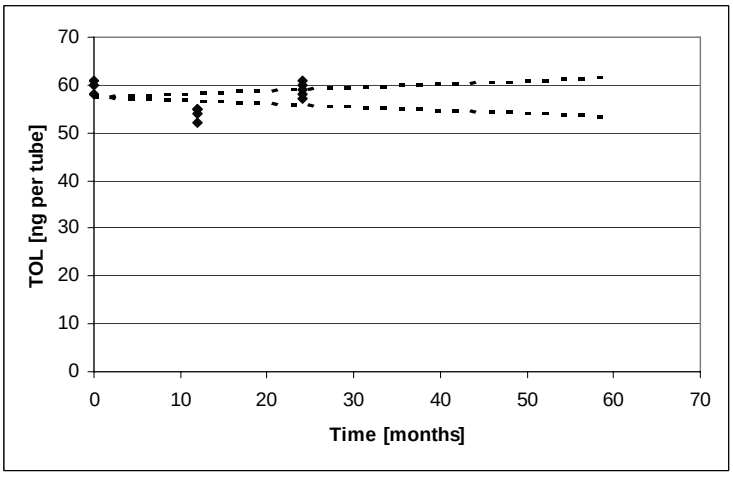


Figure 11 - Shelf-life plot for toluene in BCR-555. For a shelf-life of 48 months u_{lts} was estimated to 5.79 %.

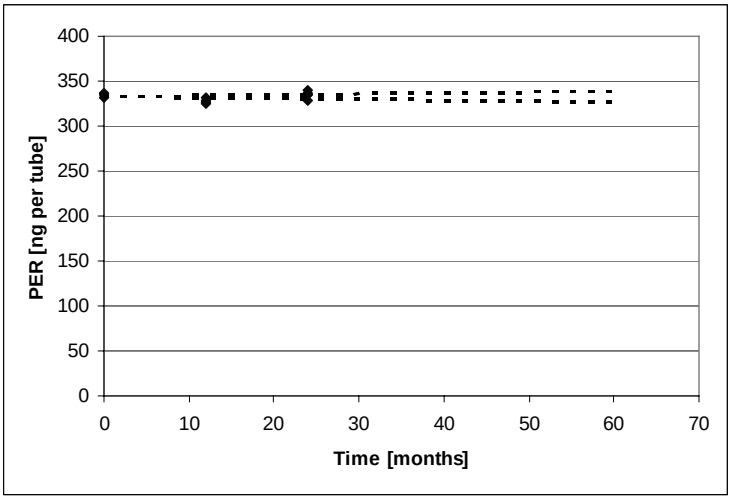


Figure 12 - Shelf-life plot for perchloroethylene in BCR-555. For a shelf-life of 48 months u_{lts} was estimated to 1.55 %.

6.3.1.4 Batch characterisation

An estimate for u_{char} was derived from the standard error obtained on the mean of laboratories means.

6.3.1.5 Uncertainty budget

Based on the uncertainty contributions mentioned in the previous sections the following uncertainty budgets are established:

Table 18 - Uncertainty budget for BCR-555

	DCM	TCE	TRI	TOL	PER
u_{bb} (s_{bb}) [in rel. %]	1.7	2.3	1.2	1.3	1.5
u^*_{bb} [in rel. %][a]	*/*	*/*	*/*	*/*	*/*
u_{lts} [in rel. %]	4.3	4.4	4.1	5.8	1.6
u_{char} [in rel. %]	3.2	2.3	1.4	1.1	1.3
coverage factor k	2	2	2	2	2
U_{CRM} [in rel. %]	11.25	10.95	8.99	12.09	5.10
Mean [in µg/kg]	315	366	388	56.4	327
Uncertainty [in µg/kg]	36	40	35	6.9	17
Rounded according to ISO 31-0 [8] and expressed in ng per tube	320 ± 40	370 ± 40	390 ± 40	57 ± 7	327 ± 17

[a] could not be established

6.3.2 Certified values

The certified values are the means of laboratory means listed in Table 18. The following masses of chlorinated hydrocarbons and toluene per tube of BCR-555 are certified:

Dichloromethane:	320	±	40	ng
1,1,1-trichloroethane:	370	±	40	ng
Trichloroethene:	390	±	40	ng
Toluene:	57	±	7	ng
Perchloroethene:	327	±	17	ng

The BCR-555 has been found to be stable for at least two years, even when stored at a temperature of 40 °C. This finding indicates a considerably longer shelf life at room temperature. It is recommended, however, that samples be stored in a clean environment at room temperature.

7. CONCLUSIONS

7.1 Preparation of calibration standards

Within the frame of this project, much effort has been put into the optimisation of procedures for the preparation of calibration standards for CHC determinations by thermal desorption - gas chromatography. Based on experience gained the following conclusion can be drawn:

- Calibration standards can be produced by liquid spiking using methanol as the solvent and gas phase spiking with equivalent results, providing the recommendations given below are adhered to.
- The purities of all compounds used in the preparation should be confirmed by analysis; particular attention should be paid to the presence and removal of water from organic solvents.
- All preparation procedures used should be made traceable to primary standards of mass and volume by applying appropriate calibrations. It is recommended to relate all volumes used to mass by repetitive weighing of volumes of the compounds to be measured. This means that volumes delivered by syringes should be sufficient to allow for accurate weighing.
- Solvent mixes for liquid spiking should be prepared by adding solvents in the reverse order of volatility.
- Excess purging of sorbent tubes should be avoided to prevent breakthrough of dichloromethane and 1,1,1-trichloroethane.

Further details on the application of liquid spiking for the preparation of calibration standards can be found in reference 7.

8. INSTRUCTIONS FOR USE

8.1 Choice of analytical method

BCR-555 is intended for uses with thermal desorption. Removing the caps should be done just prior to submitting the tube to thermal desorption. The TENAX GR sorbent should not be transferred from the tube for analysis.

In Chapter 3 of this report, and in Tables 6 and 7, useful information is given about sources of error and conditions to be used in the analytical procedure. Particularly, attention to the information about the procedures used for the preparation of calibration standards is recommended.

8.2 Use of the uncertainties

This material may be used to check the precision and the trueness of the laboratory measurement process according to ISO Guide 33 [8].

8.2.1 Assessment of precision

The precision of the measurement process is assessed by comparing the within-laboratory standard deviation (s_w) determined during the certification step. All necessary equations are listed in detail in ISO Guide 33 [8].

8.2.2 Assessment of trueness

The trueness of the measurement process is checked by comparing the average $\bar{x}$ of n measurement results with the certified value, μ. The criterion for acceptance of the results is as follows:

1. a_1 and a_2 are adjustment values chosen by the experimenter according to economical or technical limitations or stipulations.
2. 2 σ_D is the long term within-laboratory standard deviation of the user's method.

8.3 Other uses of the uncertainties

The stated uncertainties apply when the reference material is used for calibration or for verification of the validity of a calibration curve (i.e., for verification of response factors obtained).

The reference material can also be used to verify the performance of an analytical method according to requirements set by technical, economic or legislative considerations such as, e.g., laid down in Euronorm EN 482 [9].

For this purpose, the user should however, first check the repeatability of a series of measurements. Coefficients of variation should typically be within 6 % for dichloromethane and 1,1,1-trichloroethane, and within 3 % for trichloroethylene, perchloroethylene and toluene.

The accuracy of the method may then be assessed by comparison of the mean value with the certified value.

8.4 Storage

BCR-555 should be stored in a clean atmosphere at room temperature to ensure stability, for example in a closed container containing activated charcoal.

Storage at temperatures below 0°C may lead to problems due to leakage of end caps leading to losses of volatile CHC and inward migration of contaminants.

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